Step-by-Step Calculation for Cr Systematic Error Correction

To further clarify the proposed hybrid correction framework, this section provides the detailed calculation process for a 0.500 ppm Cr sample

1. Initial Bias in Basic Calibration (BC)

The normalized intensity (I_{Cr}/I_{Zn}) of the test sample was substituted into the BC equation: $I_{Cr}/I_{Zn} = 0.0891C_x + 0.0027$. The predicted concentration C_x was 1.0899 ppm, leading to a relative error (RE) of 118.0%.

2. Standard Addition Method (SAM) with Proportional Error Elimination

Matrix dilution was performed to reach the saturation interval. At a dilution volume of 3200 μL (SAC_2), the system reached a state where proportional error was minimized. The SAC_2 curve was $I_{Cr}/I_{Zn} = 0.0198C_x + 0.0140$. The concentration $C_x$was 0.7071 ppm (RE: 41.4%). While improved, the significant RE indicates the persistence of constant error.

3. Final Correction via ANCOVA and Youden Calibration

Step A (ANCOVA): Slopes of SAC_1 and SAC_2 were pooled to $b_p = 0.0210\ ppm^{-1}$. The adjusted intercept ($a_A^{'}$) for the 3200 μL system was calculated as 0.0133.

Step B (Youden Blank): The Youden blank (Y_B) was determined from the $1/N$ plot as 0.0033.

Final Integrated Calculation:

$$c_x = \frac{a_A^{'} - Y_B}{b_p} = \frac{0.0133 - 0.0033}{0.0210} \approx 0.5051\ ppm$$

The RE was reduced to 1.0%, demonstrating the necessity of correcting both error types.